# Supporting Information

# Anisotropic Alloying of Re<sub>1-x</sub>Mo<sub>x</sub>S<sub>2</sub> Nanosheets to Boost

# Electrochemical Hydrogen Evolution Reaction

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### I. Experimental Section

*Characterization*. The products were characterized by field-emission transmission electron microscopy (FE TEM, FEI TECNAI G2 200 kV, Jeol JEM 2100F, HVEM). Energy-dispersive X-ray fluorescence spectroscopy (EDX) with elemental maps was measured using a TEM (FEI Talos F200X) operated at 200 kV that equipped with high-brightness Schottky field emission electron source (X-FEG) and Super-X EDS detector system (Bruker Super-X). This EDX has powerful sensitivity and resolution in the low photon energy region. Fast Fourier-transform (FFT) images were generated by the inversion of the TEM images using Digital Micrograph GMS1.4 software (Gatan Inc.).

Inductively coupled plasma atomic emission spectroscopy (ICP-AES; Jobin Yvon Ultima 2) was also used to analyze the composition. High-resolution X-ray diffraction (XRD) patterns were obtained using the 9B and 3D beamlines of the Pohang Light Source (PLS) with monochromatic radiation ( $\lambda = 1.54595$  Å). XRD pattern measurements were also carried out in a Rigaku D/MAX-2500 V/PC using Cu K<sub>a</sub> radiation ( $\lambda = 1.54056$  Å). X-ray photoelectron spectroscopy (XPS) measurements were performed using the 8A1 and 10A2 beam lines of the PLS, as well as a laboratory-based spectrometer (Thermo Scientific Theta Probe) using a photon energy of 1486.6 eV (Al Ka). Raman spectra were measured with a micro-Raman spectrometer (Horiba ARAMIS IR2), using a diode laser with an excitation wavelength of 532 nm.

*Electrochemical Measurements*. Experiments were carried in a three-electrode cell connected to an electrochemical analyzer (CompactStat, Ivium Technologies). HER electrocatalysis (in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte) was measured using a linear sweeping from 0 to -0.6 V (vs. RHE)

with a scan rate of 2 mV s<sup>-1</sup>. A saturated calomel electrode (SCE, KCl saturated, Pine Instrument) was used as a reference electrode, and a graphite rod (6 mm dia.  $\times$  102 mm long, 99.9995%, Pine Instrument) was used as a counter electrode. The electrolyte was purged with H<sub>2</sub> (ultrahigh grade purity 99.999%) during the measurement.



**Figure E1**. CV curves for the potential of reference electrode (SCE), obtained at a scan rate of  $2 \text{ mV s}^{-1}$ , in the high-purity H<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte with a Pt wire as the working electrode.

The applied potentials (E) reported in our work were referenced to the reversible hydrogen electrode (RHE) through standard calibration. As a first step, we calibrate the potential of SCE vs. standard hydrogen electrode (SHE). Cyclic voltammetry (CV) curves were obtained at a scan rate of 2 mV s<sup>-1</sup>, in the high-purity H<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte with a Pt wire as the working electrode, as shown in **Figure E1**. The average value of the potential at which the current crossed at zero was -0.278 V. Therefore  $E_{SCE} = 0.278$  V, since E (= 0 vs. SHE) -  $E_{SCE} = -0.278$  V.

In 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte (pH 0), E (vs. RHE) = E (vs. SCE) + E<sub>SCE</sub> (= 0.278 V) + 0.0592 pH = E (vs. SCE) + 0.278 V. The overpotential ( $\eta$ ) was defined as E (vs. RHE). 4 mg Re<sub>1</sub>. <sub>x</sub>Mo<sub>x</sub>S<sub>2</sub> sample was mixed with 1 mg carbon black (Vulcan XC-72) dispersed in Nafion (20 µL) and isopropyl alcohol (0.98 mL). The catalyst materials (0.39 mg cm<sup>-2</sup>) were deposited on a glassy carbon rotating disk electrode (RDE, area = 0.1641 cm<sup>2</sup>, Pine Instrument), and a rotation speed of 1600 rpm was used for the linear sweep voltammetry (LSV) measurements. The Pt/C (20 wt.% Pt in Vulcan carbon black, Sigma-Aldrich) tested as reference sample using the same procedure. For chronoamperometric stability test, we fabricated the electrode by depositing the samples (1 mg cm<sup>-2</sup>) on 1 × 1 cm<sup>2</sup> area of hydrophilic/water proof carbon cloth (WIZMAC Co., thickness = 0.35 mm, through-plane resistance = 1 mΩ) that was cut with a size of 1 × 3 cm<sup>2</sup>.

Electrochemical impedance spectroscopy (EIS) measurements were carried out for the electrode in an electrolyte by applying an AC voltage of 10 mV in the frequency range of 100 kHz to 0.1 Hz at a bias voltage of -0.1 V (vs. RHE). To measure double-layer capacitance via CV, a potential range in which no apparent Faradaic processes occur was determined from static CV. This range is 0.1–0.2 V. All measured current in this non-Faradaic potential region is assumed to be due to double-layer capacitance. The charging current, *i*<sub>c</sub>, is then measured from CVs at multiple scan rates. The working electrode was held at each potential vertex for 10 s before beginning the next sweep. The charging current density (*i*<sub>c</sub>) is equal to the product of the scan rate (v) and the electrochemical double-layer capacitance (C<sub>dl</sub>), as given by equation  $i_c = v C_{dl}$ . The difference ( $\Delta J_{0.15}$ ) between the anodic charging and cathodic discharging currents measured at 0.15 V (vs. RHE) was used for *i*<sub>c</sub>. Thus, a plot of  $\Delta J_{0.15}$  as a function of v yields a straight line with a slope equal to 2 × C<sub>dl</sub>. The scan rates were 100–200 mV s<sup>-1</sup>.

*TOF Calculation*. The active site density and turnover frequency (TOF) have been estimated as follows. It should be emphasized that since the nature of the active sites of the catalyst is not clearly understood yet and the real surface area for the nanostructured heterogeneous catalyst is hard to accurately determine, the following result is really just an estimation.



**Figure E2**. (a) CV curves of  $\text{Re}_{1-x}\text{Mo}_x\text{S}_2$  measured at a scan rate of 50 mV s<sup>-1</sup>, in 0.1 M phosphate buffer solution (pH 7, range = -0.2 ~ 0.6 V vs. RHE). (b) Charge integrated from the CV curves *vs. x* (%).

The active sites are determined by the charge (Q) integrated from the CV curves (**Figure E2**), which was obtained in 0.1 M phosphate buffer solution (pH 7, Range =  $-0.2 \sim 0.6$  V vs. RHE). While it is difficult to assign the observed peaks to a given redox couple, the integrated charge over the whole potential range should be proportional to the total number of active sites.

The formula employed to find the number of electrochemically active sites (m) is given by

$$m = \frac{Q}{2e}$$

where Q is charge in Coulomb and the factor <sup>1</sup>/<sub>2</sub> is number of electrons taking part in oxidation/reduction process.<sup>S1,S2</sup>

The TOF can be caculated from the total number of hydrogen gas (H<sub>2</sub>) molecules ( $n_{H2}$ ) turns overs at a required potential as follows.

TOF = 
$$n_{\rm H2}/m = J \,(\text{mA cm}^{-2}) \times 3.12 \times 10^{15} \,(\text{H}_2 \,\text{s}^{-1} \,\text{per mA cm}^{-2}) \times \text{electrode area} \,(= 0.1641 \,\,\text{cm}^2)/m$$

where  $n_{\text{H2}}$  was calculated from the current density (*J*) according to  $n_{\text{H2}} = J (\text{mA cm}^{-2})/1000 \text{ mA}$ × 1 (C s<sup>-1</sup>) × 1 mol e<sup>-</sup>/96486 C × 1 mol H<sub>2</sub>/2 mol e<sup>-</sup> × 6.022 × 10<sup>23</sup> H<sub>2</sub> molecules/1 mol H<sub>2</sub> × electrode area =  $J (\text{mA cm}^{-2}) \times 3.12 \times 10^{15} (\text{H}_2 \text{ s}^{-1}) \times \text{electrode area} (= 0.1641 \text{ cm}^2).$ 

We summarized the results in Table E.

**Table E**. TOF of Re<sub>1-x</sub>Mo<sub>x</sub>S<sub>2</sub> samples at  $\eta = 0.15$  V, calculated using the density of surface active (*m*).

Samples	J (mA cm <sup>-2</sup> ) at 0.15 V	<i>n</i> <sub><i>H</i>2</sub>	<i>Q</i> (mC)	т	TOF (H <sub>2</sub> s <sup>-1</sup> )
$x = 0\% (\text{ReS}_2)$	2.42	$1.23 \times 10^{15}$	2.85	$8.89 \times 10^{15}$	0.14
20%	2.78	$1.42 \times 10^{15}$	4.34	$1.35 \times 10^{16}$	0.10
40%	8.35	$4.27 \times 10^{15}$	5.59	$1.74 \times 10^{16}$	0.24
50%	80.12	$4.10 \times 10^{16}$	6.15	$1.91 \times 10^{16}$	2.14
60%	17.45	$8.91 \times 10^{15}$	7.34	$2.29 \times 10^{16}$	0.39
80%	11.81	$6.04 \times 10^{15}$	7.83	$2.44 \times 10^{16}$	0.25
100% (MoS <sub>2</sub> )	3.27	$1.67 \times 10^{15}$	9.12	$2.84 \times 10^{16}$	0.06

*Computational details*. First-principles calculations were performed via spin-polarized density functional theory (DFT), as implemented in the Vienna *ab initio* simulation package (VASP).<sup>S3,S4</sup> The electron-ion interactions were described using the projector-augmented wave (PAW) method with a plane-wave kinetic energy cutoff of 400 eV. The effect of attractive van der Waals interactions were included using Grimme's correction for the PBE-D3 method.<sup>S5</sup>

The crystal structure was prepared using a supercell of one (3×3)  $\text{Re}_{1-x}\text{Mo}_x\text{S}_2$ , which is equivalent to (6×6)  $\text{MoS}_2$ . The structural optimization was performed until the average force was < 0.02 eV per (Å atom) and the final energy change was < 10<sup>-4</sup> eV per atom. Lattice constants were optimized using the PBE-D3 exchange-correlation functional. Monkhorst-Pack *k*-point sampling of 3×3×5 were used for the geometry optimization.

We employed a slab geometry in which a supercell included one (3×3) Re<sub>1-x</sub>Mo<sub>x</sub>S<sub>2</sub> layer. A vacuum space of 20 Å was used along the Z(//c) direction (perpendicular to the slabs) to ensure that no appreciable interaction occurred between adjacent images. Structural optimization was performed until the average force was < 0.03 eV/Å and the total energy converged within 10<sup>-4</sup> eV/atom. A Monkhorst-Pack *k*-point sampling of 3×3×1 was used for slab geometry, while only  $\Gamma$ -point was used for molecules. All atoms belonging to two bottom-most sublayers were fixed, while all other atoms were allowed to relax freely.

Under the standard condition, the HER includes two steps: a H adsorption on the catalyst (\*) in the Volmer reaction, followed by the Heyrovsky/Tafel reaction releasing the hydrogen molecule  $(1/2 H_2 + *)$ . Therefore, we can construct Gibbs free energy profile along the reaction coordinate by calculating relative free energy of the reactant and that of the reaction intermediate produced in Volmer reaction, i.e., H\*. Here, the asterisk (\*) designates that the hydrogen atom (H) was adsorbed on the catalytic surface. Gibbs free energy can be calculated according to:

$$G = E_{DFT} + E_{ZPE} + H_{corr} - TS$$

where  $E_{DFT}$  is the total energy obtained from the DFT calculation,  $E_{ZPE}$  is the zero point energy

 $H_{corr} = \int_{0}^{298} C_V dT$ correction, and is the reaction enthalpy change from 0 to 298 K, and *TS* is the entropy correction based on Debye model. H<sub>2</sub> molecule was treated as an ideal gas, while the adsorbed H\* were treated using the harmonic approximation. As described in our previous work,<sup>S6</sup> the PBE/6-311++G\*\* level was employed using Gaussian09 for the frequency calculation of gas molecule.<sup>S7</sup>

#### **II. Supplementary Tables**

**Table S1**. Composition determined using XPS, EDX, and Inductively coupled plasma atomic emission spectrometry (ICP AES) analysis data of  $\text{Re}_{1-x}\text{Mo}_x\text{S}_2$  samples. The three data gave the consistent *x* values as shown the graphs.

Samples		[Mo]/([]	Mo]+[Re])	[S]/([Mo]+[Re])			
x (%)	XPS	EDX	<b>ICP-AES</b>	Avg.	XPS	EDX	Avg.
0	0	0	0	0	1.79	1.82	1.80
20	22	19	19.85	20	1.81	1.82	1.81
40	42	38	39.76	40	1.80	1.83	1.81
50	52	51	48.77	50	1.82	1.82	1.81
60	61	58	59.00	59	1.81	1.84	1.82
80	81	78	78.52	79	1.81	1.83	1.82
100	100	100	100	100	1.81	1.82	1.81



Sample (Mo K edge)	Scattering Path	R (Å) <sup>a</sup>	CN <sup>b</sup>	$\Delta E (eV)^{c}$	$\sigma^2({\rm \AA}^2)^d$
MoS.	Mo-S	2.414	6.0	0.082	0.0073
10002	Mo-Mo	2.795	2.0	7.369	0.0052
Rea Mos S.	Mo-S	2.405	$6.0 \pm 0.5$	0.128	0.0087
ICC0.21VIO0.852	Mo-Mo	2.803	$1.1 \pm 0.9$	6.382	0.0065
Rea Moa S.	Mo-S	2.385	$6.5 \pm 0.7$	-2.287	0.0105
ICC0.51V100.502	Mo-Mo	2.952	$1.2 \pm 0.8$	3.086	0.0098
Rea Moa S.	Mo-S	2.533	$6.6 \pm 0.6$	-5.066	0.0116
100.810100.252	Mo-Mo	2.952	$1.8 \pm 0.9$	1.458	0.0128
Sample	Scattering	<b>D</b> (Å)a	CNIb		$-2(\hat{x}^2)d$
Sample (Re L <sub>3</sub> edge)	Scattering Path	R (Å) <sup>a</sup>	CN <sup>b</sup>	ΔE (eV) <sup>c</sup>	$\sigma^2({\rm \AA}^2)^d$
Sample (Re L <sub>3</sub> edge)	Scattering Path Re-S	R (Å) <sup>a</sup> 2.387	$CN^b$ $6.6 \pm 0.4$	ΔE (eV) <sup>c</sup> 5.598	$\sigma^2 (Å^2)^d$ 0.0070
$\frac{\text{Sample}}{(\text{Re } \text{L}_3 \text{ edge})}$ $\text{Re}_{0.2}\text{Mo}_{0.8}\text{S}_2$	Scattering Path Re-S Re-Re	R (Å) <sup>a</sup> 2.387 2.760	$\frac{\text{CN}^{\text{b}}}{6.6 \pm 0.4}$ $1.9 \pm 0.9$	ΔE (eV) <sup>c</sup> 5.598 3.813	$\frac{\sigma^2 (\text{\AA}^2)^d}{0.0070} \\ 0.0132$
$\frac{\text{Sample}}{(\text{Re } \text{L}_3 \text{ edge})}$ $\frac{\text{Re}_{0.2}\text{Mo}_{0.8}\text{S}_2}{\text{Re}_{0.2}\text{Mo}_{0.8}\text{S}_2}$	Scattering Path Re-S Re-Re Re-S	R (Å) <sup>a</sup> 2.387 2.760 2.370	$\frac{\text{CN}^{\text{b}}}{6.6 \pm 0.4}$ $\frac{1.9 \pm 0.9}{6.3 \pm 0.5}$	ΔE (eV) <sup>c</sup> 5.598 3.813 5.514	$\begin{array}{c} \sigma^2 ( {\rm \AA}^2)^{\rm d} \\ \hline 0.0070 \\ \hline 0.0132 \\ \hline 0.0074 \end{array}$
$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	Scattering Path Re-S Re-Re Re-S Re-Re	R (Å) <sup>a</sup> 2.387 2.760 2.370 2.776	$\frac{\text{CN}^{\text{b}}}{6.6 \pm 0.4}$ $1.9 \pm 0.9$ $6.3 \pm 0.5$ $1.9 \pm 0.9$	ΔE (eV) <sup>c</sup> 5.598 3.813 5.514 6.381	$\begin{array}{c} \sigma^2({\rm \AA}^2)^{\rm d} \\ \hline 0.0070 \\ 0.0132 \\ \hline 0.0074 \\ 0.0068 \end{array}$
$\frac{\text{Sample}}{(\text{Re } \text{L}_3 \text{ edge})}$ $\frac{\text{Re}_{0.2}\text{Mo}_{0.8}\text{S}_2}{\text{Re}_{0.5}\text{Mo}_{0.5}\text{S}_2}$	Scattering Path Re-S Re-Re Re-S Re-Re Re-S	R (Å) <sup>a</sup> 2.387 2.760 2.370 2.776 2.365	$CN^{b}$ 6.6 ± 0.4 1.9 ± 0.9 6.3 ± 0.5 1.9 ± 0.9 6.5 ± 0.4	ΔE (eV) <sup>c</sup> 5.598 3.813 5.514 6.381 6.231	$\begin{array}{c} \sigma^2({\rm \AA}^2)^d \\ \hline 0.0070 \\ 0.0132 \\ \hline 0.0074 \\ \hline 0.0068 \\ \hline 0.0070 \end{array}$
Sample (Re L3 edge) Re0.2Mo0.8S2 Re0.5Mo0.5S2 Re0.8Mo0.2S2	Scattering Path Re-S Re-Re Re-S Re-Re Re-S Re-Re	R (Å) <sup>a</sup> 2.387 2.760 2.370 2.776 2.365 2.776	$CN^{b}$ 6.6 ± 0.4 1.9 ± 0.9 6.3 ± 0.5 1.9 ± 0.9 6.5 ± 0.4 2.0 ± 0.7	ΔE (eV) <sup>c</sup> 5.598 3.813 5.514 6.381 6.231 3.822	$\begin{array}{c} \sigma^2({\rm \AA}^2)^{\rm d} \\ \hline 0.0070 \\ 0.0132 \\ 0.0074 \\ 0.0068 \\ 0.0070 \\ 0.0059 \end{array}$
$\frac{\text{Sample}}{(\text{Re } \text{L}_3 \text{ edge})}$ $\frac{\text{Re}_{0.2}\text{Mo}_{0.8}\text{S}_2}{\text{Re}_{0.5}\text{Mo}_{0.5}\text{S}_2}$ $\frac{\text{Re}_{0.8}\text{Mo}_{0.2}\text{S}_2}{\text{Re}_{0.8}\text{Mo}_{0.2}\text{S}_2}$	Scattering Path Re-S Re-Re Re-S Re-Re Re-S Re-Re Re-S Re-S	R (Å) <sup>a</sup> 2.387 2.760 2.370 2.776 2.365 2.776 2.366	$CN^{b}$ $6.6 \pm 0.4$ $1.9 \pm 0.9$ $6.3 \pm 0.5$ $1.9 \pm 0.9$ $6.5 \pm 0.4$ $2.0 \pm 0.7$ $6.0$	ΔE (eV) <sup>c</sup> 5.598 3.813 5.514 6.381 6.231 3.822 2.923	$\begin{array}{c} \sigma^2({\rm \AA}^2)^{\rm d} \\ \hline 0.0070 \\ 0.0132 \\ 0.0074 \\ 0.0068 \\ \hline 0.0070 \\ 0.0059 \\ 0.0068 \end{array}$

**Table S2.** Fitting parameters of FT EXAFS data (Figures 2f and 2g) for the  $Re_{1-x}Mo_xS_2$  samples.

<sup>*a*</sup> Distance between scattering atoms. <sup>*b*</sup> Coordination number.

<sup>*c*</sup> Edge energy shift, representing between the energy grids of experimental and theoretical data. <sup>*d*</sup> Debye-Waller factor, which measure the static and thermal disorder, is larger for the alloy samples than MoS<sub>2</sub>.

Ref. No.	Ref. in Text <sup>a</sup>	Materials	$\eta_{J=10} (mV)$ at 10 mA cm <sup>-2</sup>	Tafel slope (mV dec <sup>-1</sup> )	TOF (H <sub>2</sub> s <sup>-1</sup> )
S8	5	Exfoliated ReS <sub>2</sub>	260	75	
S9	6	$ReS_2$ on carbon foam	450		
S10	7	ReS <sub>2</sub> /Au	200	84	
S11	8	ReS <sub>2</sub> microsphere	>500	675	
S12	10	defect-rich ReS <sub>2</sub> /carbon fiber paper	120	137	
S13	11	ReS <sub>2</sub> /carbon fiber	220 (dark) 170 (light)	80 (dark) 77 (light)	1.7 at 0.3 V
S14	12	Re-vacant ReS <sub>2</sub> /Si	147	69	10 at 0.14 V
S15	13	ReS <sub>2</sub> ReSSe	320 84	106.9 50.1	
S16	15	$\begin{array}{c} ReS_2 \\ ReSe_{1.78}S_{0.22}/carbon \\ fiber paper \end{array}$	298 123	133 84	
S17	16	$Mo_{0.45}Re_{0.55}S_2$	169	56	3.48 at 0.3 V
S18	18	ReS <sub>2</sub> /carbon fiber	173	69.5	
S19	22	ReS <sub>2</sub> @CNT	196		
S20	26	ReS <sub>2</sub> /3D-printed electrode	288	147	
S21	27	ReS <sub>2</sub> /ReO <sub>2</sub> /Graphene -Polyimide film	150	65	
S22	28	N-ReS <sub>2</sub> /CC	90 (pH 14)	85	
S23	33	2%-Co doped ReS <sub>2</sub>	149	107	
S24	34	$ReS_2/CoS_2$	114	63.7	
This work		$Mo_{0.5}Re_{0.5}S_2$	98	54	2.14 at 0.15 V

Table S3. Comparison of HER performance (in pH 0) of  $ReS_2$ -based catalysts in the literatures.

<sup>*a*</sup> Reference number in text.

x (%)	Phase <sup>a</sup>	$E_{rel}(eV)^b$	$C_{VS}(\%)^c$	<i>a</i> , <i>b</i> , <i>c</i> (Å), $\alpha$ , $\beta$ , $\gamma$ (°) <sup><i>d</i></sup>
	1T''	0	0	19.48, 19.16, 6.44, 105.09, 91.88, 118.83
0	1T'	11.47	0	19.62, 18.9, 6.17, 119
0	1T''	0	5.6	19.33, 18.92, 6.44, 104.92, 91.80, 118.72
	1T′	10.45	5.6	19.62, 18.9, 6.17, 119
14	1T''	0	0	19.46, 19.26, 6.40, 105.18, 91.44, 118.97
	1T''	0	0	19.54, 19.16, 6.38, 104.76, 92.13, 119.10
	1T'	0.61	0	19.67, 19.19, 6.0, 119
50	2H	4.52	0	19.09, 19.09, 6.68, 120
30	1T''	0	5.6	19.38, 19.16, 6.43, 105.14, 92.15, 119.60
	1T'	0	5.6	19.64, 19.05, 6.06, 119
	2H	1.42	5.6	18.84, 18.84, 6.66, 120
	1T''	0	0	19.59, 19.11, 6.36, 104.45, 93.33, 119.23
	1T'	0.24	0	19.65, 19.16, 5.88, 119
96	2H	-14.15	0	18.94, 18.94, 6.13, 120
80	1T''	0	5.6	19.57, 19.11, 6.41, 104.45, 95.55, 119.25
	1T′	-0.47	5.6	19.59, 19.27, 5.90, 119
	2H	-14.17	5.6	18.76, 18.76, 6.18, 120
	2H	0	0	18.97, 18.97, 6.14, 120
100	1T'	20.45	0	19.56, 19.02, 6.04, 119
100	2H	0	5.6	18.83, 18.83, 6.15, 120
	1T'	16.78	5.6	19.42, 19.13, 5.90, 119

**Table S4**. Calculated relative energy of 1T", 1T', and 2H phase  $\text{Re}_{1-x}\text{Mo}_x\text{S}_2$  at x = 0% (ReS<sub>2</sub>), 14%, 50%, 86%, and 100% (MoS<sub>2</sub>) and lattice parameters.

<sup>*a*</sup> Crystal phase.

<sup>b</sup> Relative energy of the corresponding supercell with respect to that of the most stable phase.

<sup>c</sup> The concentration of S vacancies. See the text for definition.

<sup>*d*</sup> The optimized lattice parameters of a supercell in each phase. The  $\alpha$ ,  $\beta$ , and  $\gamma$  angles are those between the *b*-*c*, *a*-*c*, and *a*-*b* axes, respectively. For the 1T'' phase, all of *a*, *b*, *c*,  $\alpha$ ,  $\beta$ , and  $\gamma$  values are shown in sequence. The  $\alpha$  and  $\beta$  values are not shown for the 1T' and 2H phases, since both of them are 90°. The *c* constant of the 2H is divided by two to compare with other phases.

**Table S5.** Calculated thermodynamic parameters for the Gibbs free energy ( $\Delta G_{H^*}$ ) of the intermediate. They include zero-point energy

29	18 <b>F</b>
()	$C_v dT$ )

correction ( $E_{ZPE}$ ), enthalpy correction,  $H_{corr}$  <sup>0</sup>, entropy correction (TS), and Gibbs free energy change ( $\Delta G_{H^*}$ ) for a H atom adsorption on the slab geometry of a (3×3) Re<sub>1-x</sub>Mo<sub>x</sub>S<sub>2</sub> in the appropriate phase at various *x* values. ( $\Delta$  is defined as the quantity of the reaction intermediate minus the corresponding quantity of the reactant). All energies are in eV.

x(%)	Phase <sup>a</sup>	$C_{VS}(\%)^b$	Sites	$\Delta E_{DFT}$	E <sub>ZPE</sub>	H <sub>corr</sub>	TS	$\Delta E_{ZPE}$	$\Delta H_{corr}$	$T\Delta S_{\mathrm{H}*}$	$\Delta G_{\mathrm{H}^*}$
0	1T″	0	-	1.17	0.22	0.01	0.01	0.085	-0.02	-0.19	1.42
			1	0.03	0.23	0.01	0.01	0.095	-0.02	-0.19	0.30
14	1T″	0	2	0.58	0.20	0.01	0.01	0.065	-0.02	-0.18	0.81
			3	0.68	0.20	0.01	0.01	0.065	-0.02	-0.19	0.92
			1	-0.16	0.23	0.01	0.01	0.095	-0.02	-0.19	0.11
	1T″	0	2	0.26	0.23	0.01	0.01	0.095	-0.02	-0.19	0.52
50			3	0.52	0.21	0.01	0.02	0.075	-0.02	-0.18	0.75
50	50		1	-0.32	0.23	0.01	0.01	0.095	-0.02	-0.19	-0.05
	1T″	5.6	2	-0.63	0.17	0.00	0.01	0.035	-0.03	-0.19	-0.43
			3	0.69	0.22	0.01	0.01	0.085	-0.02	-0.19	0.95
	1T'	0	-	-0.09	0.23	0.01	0.01	0.095	-0.02	-0.19	0.17
100	1T'	5.6	-	-0.16	0.23	0.01	0.01	0.075	-0.02	-0.19	0.08
	2H	0	-	1.57	0.20	0.01	0.02	0.065	-0.02	-0.18	1.79
H <sub>2</sub>	gas		-	-	0.27	0.06	0.40	-		-	-

<sup>*a*</sup> Most stable phase  $\text{Re}_{1-x}\text{Mo}_x\text{S}_2$  with x = 0% (ReS<sub>2</sub>), 14%, 50%, and 100% (MoS<sub>2</sub>)

<sup>*b*</sup> Concentration of S vacancies in %.

#### **III. Supplementary Figures**



**Fig. S1** Electron spin (or paramagnetic) resonance (ESR or EPR) spectra for  $\text{Re}_{1-x}\text{Mo}_x\text{S}_2$  at x = 0%, 20%, 50%, 80%, and 100%.

ESR measurements were performed on a Bruker EMX-Plus spectrometer at room temperature. Ten milligrams of as-prepared samples were loaded in a quartz tube. The microwave frequency v was 9.64 GHz (X-band), and the *g*-factor was calculated as  $hv = g \times \mu_B \times B$ , where  $\mu_B$  and B are the Bohr magneton and magnetic field, respectively. All samples exhibit a strong S shape signal (per mg) at 344 mT (g = 2.00), due to the S vacancies.



**Fig. S2** (a) SEM images of  $\text{Re}_{1-x}\text{Mo}_x\text{S}_2$  samples with x = 0%, 20%, 40%, 50%, 60%, 80%, and 100%. They all consisted of the flower-like nanosheets. (b) Lattice-resolved TEM images of  $\text{Re}_{0.5}\text{Mo}_{0.5}\text{S}_2$  (x = 50%),  $\text{ReS}_2$  (x = 0%), and  $\text{MoS}_2$  (x = 100%). (c) HAADF-STEM images and EDX elemental mapping of  $\text{Re}_{1-x}\text{Mo}_x\text{S}_2$  samples with x = 0%, 20%, 40%, 60%, 80%, and 100%. The Re, Mo, and S elements distributed uniformly over entire sample.



**Fig. S3** (a) XRD pattern of Re<sub>1-x</sub>Mo<sub>x</sub>S<sub>2</sub> samples, after annealing at 400 °C (for 1 h) under Ar flow. The reference peaks correspond to the 1T'' ReS<sub>2</sub> (a = 6.49 Å, b = 6.20 Å, c = 6.70 Å,  $\alpha = 105.09^\circ$ ,  $\beta = 91.88^\circ$ ,  $\gamma = 118.83^\circ$ ), 2H MoS<sub>2</sub> (a = 3.25 Å and c = 12.9 Å), and monoclinic (1T') phase MoS<sub>2</sub> (a = 6.52 Å, b = 3.17 Å, c = 12.9 Å, and  $\gamma = 119^\circ$ ). The peak at 2 $\theta = 55-67$  degrees are magnified. The data points (circles) are fitted by a Voigt function, and the sum of the resolved bands is represented by the black line. (b) Raman spectrum of Re<sub>1-x</sub>Mo<sub>x</sub>S<sub>2</sub> samples before/after annealing under Ar flow at 400 °C. The excitation source is 532 nm diode laser.

After annealing, MoS<sub>2</sub> show the peaks matched to the 2H phase MoS<sub>2</sub>. The (002) position appears at  $2\theta = 13.5$  degrees (°), which is the same position of ReS<sub>2</sub> (001) peak. The peak at 59.1° is assigned to the (112)<sub>2H</sub> peak. The ReS<sub>2</sub> shows the peak at 57.8°, which is assigned to the (04)<sub>1T"</sub> (red). At x = 40%, the resolved band (blue) at 57.2° was assigned to the (440) peak of 1T' MoS<sub>2</sub>. At x = 50-80%, the new peak (orange) at 59.1° is assigned to the (112)<sub>2H</sub>. As xincreases to 50%, the intensity of (440)<sub>1T'</sub> peak decreases, while that of (112)<sub>2H</sub> peak increases. Therefore, the major phase is 1T'' ReS<sub>2</sub> at x = 0-40%, and 2H MoS<sub>2</sub> at x = 60%-100%. Most of 1T' phase MoS<sub>2</sub> converted to the 2H phase MoS<sub>2</sub>.

ReS<sub>2</sub> exhibits the typical Raman peaks, corresponding to those in 1T" phase ReS<sub>2</sub>. Many peaks arise from the complexity of lattice vibrations in 1T" phase ReS<sub>2</sub>, consistently with the previous works.<sup>S25,S26</sup> The peak at 150 cm<sup>-1</sup> is assigned to  $E_g$ -like vibrational mode (in-plane vibration), and the peak at 210 cm<sup>-1</sup> to A<sub>g</sub>-like modes (out-of-plane vibration). At the higher *x*, the peak intensity decreases gradually. Before annealing, as-grown MoS<sub>2</sub> exhibits two

characteristic Raman peaks of the 2H phase MoS<sub>2</sub> at 406 and 380 cm<sup>-1</sup>, corresponding to the out-of-plane  $A_g$  and in-plane  $E_{2g}^1$  vibration modes, respectively.<sup>S27</sup> The peak at 284 cm<sup>-1</sup> was assigned to the  $E_{1g}$  mode. x = 80% and MoS<sub>2</sub> samples shows the unique Raman peaks of 1T' phase MoS<sub>2</sub>: J<sub>1</sub> peak at 150 cm<sup>-1</sup>, J<sub>2</sub> peak at 199 cm<sup>-1</sup>, and J<sub>3</sub> peak at 337 cm<sup>-1</sup>. Therefore the Raman data of as-grown samples indicate that (i) at x = 0.40%, the 1T'' phase ReS<sub>2</sub> phase is a dominant phase; (ii) at x = 80% and 100%, the 1T' and 2H phase MoS<sub>2</sub> coexist, which are consistent with the XRD data. After annealing, the peaks of 1T' phase MoS<sub>2</sub> disappear, due to the phase conversion into 2H phase MoS<sub>2</sub>. The peaks of ReS<sub>2</sub> becomes stronger. These Raman data are also consistent with the XRD data.



**Fig. S4** Fine-scan XPS peaks of S  $2p_{3/2}$  and  $2p_{1/2}$  of Re<sub>1-x</sub>Mo<sub>x</sub>S<sub>2</sub> (x = 0%, 20%, 40%, 50%, 60%, 80%, and 100%). The raw XPS data (open circles) are fitted by a Voigt function, and the sum of the resolved bands is represented by the black line. The position of neutral S (S<sup>0</sup>  $2p_{3/2}$  at 164.0 eV) is marked by dotted vertical lines.

The S  $2p_{3/2}$  and  $2p_{1/2}$  peaks (separated by 1.2 eV) of ReS<sub>2</sub> appear as a broad peak centered at 162.5 eV, which is redshifted from the  $2p_{3/2}$  peak of neutral S at 164.0 eV (S<sup>0</sup>, marked by dotted line). The broad peak was resolved into four bands: two pink S1 bands (at 161.7 and 162.7 eV) for the S<sup>2-</sup> of Re-S bonding structures, and two blue S2 bands (at 162.7 and 163.7 eV) for the bridge (S<sub>2</sub><sup>2-</sup>) anions at the defects. As *x* increases to 50%, the peak redshifts to 161.5 eV, in the same order as for the Re and Mo binding energies, due to the incorporation of 1T' phase. At *x* = 20%-50%, the pink S1 bands (at 161.4 and 162.6 eV) and the blue S2 bands (at 162.1 and 163.3 eV) are ascribed to the S<sup>2-</sup> and S<sub>2</sub><sup>2-</sup> of Re-S/Mo-S in the 1T'' phase, respectively. For *x* = 60%~100%, the peaks were resolved into six bands (S1~ S3) with the additional S3 band: two green S3 bands (at 161.0 and 162.1 eV) for the 1T' phase S<sup>2-</sup> of Mo-S bonds, two pink S2 bands (at 161.4 and 162.6 eV) for the 1T' phase S<sup>2-</sup> of Mo-S bonds, two purple S1 bands (at 161.9 and 163.0 eV) for the 2H phase S<sup>2-</sup> of Mo-S bonds.



**Fig. S5** Nyquist plots for EIS measurements of  $\text{Re}_{1-x}\text{Mo}_x\text{S}_2$  samples (with x = 0%, 20%, 40%, 50%, 60%, 80%, and 100%), using the frequency in the range from 100 kHz to 0.1 Hz at a representative potential of -0.1 V (vs. RHE). The plots in the right panel corresponds to the magnified one in the marked area on the left plot. The modified Randles circuit for fitting is shown. The data points and the fitting curves are represented by the circles and black line, respectively.

Electrochemical impedance spectroscopy (EIS) measurements of the samples were performed using a 100 kHz–0.1 Hz frequency range and an amplitude of 10 mV at  $\eta = 0.1$  V. In the highfrequency limit and under non-Faradaic conditions, the electrochemical system is approximated by the modified Randles circuit shown in the inset, where R<sub>s</sub> denotes the solution resistance, CPE is a constant-phase element related to the double-layer capacitance, and R<sub>ct</sub> is the charge-transfer resistance from any residual Faradaic processes. A semicircle in the lowfrequency region of the Nyquist plots represents the charge transfer process, with the diameter of the semicircle reflecting the charge-transfer resistance. The real (Z') and negative imaginary (-Z'') components of the impedance are plotted on the *x* and *y* axes, respectively. The simulation of the EIS spectra using an equivalent circuit model allowed us to determine the charge transfer resistance,  $R_{ct}$ , which is a key parameter for characterizing the catalyst-electrolyte charge transfer process. The fitting parameters are listed below. The  $R_{ct}$  values of  $Re_{1-x}Mo_xS_2$  follow the order consistently with the HER performance.





**Fig. S6** Cyclic voltammetry (CV) curves of Re<sub>1-x</sub>Mo<sub>x</sub>S<sub>2</sub> samples with x = 0 (ReS<sub>2</sub>), 20%, 40%, 50%, 50%, 80%, and 100% (MoS<sub>2</sub>), in a non-Faradaic region (0.1-0.2 V vs. RHE), at 100-200 mV s<sup>-1</sup> scan rates (with a step of 20 mV s<sup>-1</sup>) and in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. Difference ( $\Delta J$ ) between the anodic charging and cathodic discharging currents measured at 0.15 V (vs. RHE) and plotted as a function of the scan rate. The value in parenthesis represents the double-layer capacitance (C<sub>dl</sub>), obtained by the half of the linear slope. The C<sub>dl</sub> value *vs. x* is plotted to show a maximum value at x = 50%.

CV data were measured at 0.1-0.2 V, in a non-Faradaic region. The C<sub>dl</sub> was obtained as the slope (half value) of a linear fit of  $\Delta J vs$ . scan rate (100-200 mV s<sup>-1</sup>), where  $\Delta J$  is the difference between the anodic charging (positive value) and cathodic discharging currents (positive value). The C<sub>dl</sub> value in a unit of mF cm<sup>-2</sup> is 11.1 (for x = 0%, ReS<sub>2</sub>), 20.7 (for x = 20%), 24.8 (for x = 40%), 40.4 (for x = 50%), 40.2 (for x = 60%), 36.0 (for x = 80%), and 20.8 (for x = 100%, MoS<sub>2</sub>). The C<sub>dl</sub> value increases with increasing x until 50%, and then decrease afterwards, consistently with the composition dependence of HER performance. Therefore, the double-layer capacitance determines the HER catalytic activity of Re<sub>1-x</sub>Mo<sub>x</sub>S<sub>2</sub> samples.



**Fig. S7** (a) HAADF-STEM image, EDX elemental mapping, and EDX spectrum of x = 50% sample after 12 h HER CA test. The nanosheet morphology remains the same after the HER. The EDX mapping shows that the Mo, Re, and S atoms distribute homogeneously over the entire samples. The EDX spectrum shows x = 50%, which remain the same as that of before. (b) XRD patterns of the sample (deposited on carbon cloth) remain the same after the HER. (c) Fine-scan Re 4*f*, Mo 3*d*, and S 2*p* peaks before and after HER. The experimental data (open circles) are fitted by a Voigt function, and the sum of the resolved bands is represented by a black line. The peak profile remains the same after the HER. This XPS data was measured by a laboratory-based spectrometer using a photon energy of 1486.6 eV (Al K $\alpha$ ), while the data shown in the text was measured by 8A1 beam lines of the PLS using a photon energy of 600 eV. Therefore, the peak shapes are different from those in Figure 2.



**Fig. S8** Crystal structures of four configurations of  $Re_{31}Mo_5S_{72}$  (corresponding to x = 14%),  $Re_{18}Mo_{18}S_{72}$  (corresponding to x = 50%), and  $Re_5Mo_{31}S_{72}$  (corresponding to x = 86%) which were built from  $(3 \times 3 \times 1)$  supercell of 1T'' phase  $ReS_2$ . The supercell contains one layer of  $Re_{31}Mo_5S_{72}$  with five Mo atoms. On the other hand, the supercell contains one layer of  $Re_5Mo_{31}S_{72}$  with five Re atoms. The relative energy ( $E_{rel}$ ) per supercell is given in eV with respect to the most stable configuration. Green, purple, and yellow balls represent Re, Mo, and S atoms, respectively.



**Fig. S9** Crystal structures of configurations of  $\text{Re}_{36}\text{S}_{72}$  (x = 0%),  $\text{Re}_{31}\text{Mo}_5\text{S}_{72}$  (14%),  $\text{Re}_{18}\text{Mo}_{18}\text{S}_{72}$  (x = 50%), and  $\text{Re}_5\text{Mo}_{31}\text{S}_{72}$  (x = 86%) with S vacancies ( $C_{VS} = 5.6\%$ ) built from ( $3 \times 3 \times 1$ ) supercell of 1T" phase as compared to the most stable pristine configuration (the first one). The relative energy ( $E_{rel}$ ) per supercell is given in eV with respect to the most stable configuration. Green, purple, and yellow balls represent Re, Mo, and S atoms, respectively. A supercell contains four S vacancies, as marked by red dashed circles.



**Fig. S10** Crystal structures of  $\text{Re}_{36}\text{S}_{68}(x = 0\%)$ ,  $\text{Re}_{18}\text{Mo}_{18}\text{S}_{68}(50\%)$ ,  $\text{Re}_5\text{Mo}_{31}\text{S}_{72}(x = 86\%)$ ,  $\text{Mo}_{36}\text{S}_{68}(x = 100\%)$ , with S vacancies ( $C_{VS} = 5.6\%$ ) built from (3 × 6 × 1) supercell of 1T' phase as compared to the most stable pristine configuration (the first one). A supercell contains four S vacancies, as marked by red circles. The relative energy ( $E_{rel}$ ) per supercell is given in eV with respect to the most stable configuration. Green, purple, and yellow balls represent Re, Mo, and S atoms, respectively.







**Fig. S11** Crystal structures of the most stable configurations of  $\text{Re}_{18}\text{Mo}_{18}\text{S}_{72}$  (corresponding to x = 50%),  $\text{Re}_5\text{Mo}_{31}\text{S}_{72}$  (corresponding to x = 86%), and  $\text{Mo}_{36}\text{S}_{72}$  (corresponding to x = 100%) with no S vacancy and 5.6% S vacancies (C<sub>VS</sub>), which were built from (6 × 6 × 1) supercell of 2H phase. Green, purple, and yellow balls represent Re, Mo, and S atoms, respectively. Four S vacancies are marked by red dotted circles.



**Fig. S12** Crystal structures of the most stable configurations of  $N_2H_5$ -intercalated  $Mo_{32}S_{60}$  complexes, which were built from 1T' (2 × 4× 2) phase and 2H phase (4 × 4 × 2) supercell with S vacancies ( $C_{VS} = 6.3\%$ ). Purple, yellow, blue and greyish-white balls represent Mo, S, N, and H atoms, respectively. The S vacancies are marked by red circles. Relative energy of 2H vs. 1T' phase decreases from 18.18 eV (for perfect) to 14.01 eV for  $C_{VS} = 6.3\%$  and  $N_2H_5$  intercalation.

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